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Preparations, Characteristics and Applications

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TITANIUM NITRIDE COATINGS
PREPARATION, CHARACTERISTICS AND APPLICATIONS

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1. INTRODUCTION

Titanium nitride (TiN) is a material with a very high melting point (2950^{o}C), high hardness (16700 MPa) and good chemical stability (Kirk-Othmer, 1983). These caracteristics, as well as high wear resistance and golden-yellow colour, have led to an increasing interest for application of TiN in the form of thin protective and/or decorative coatings.

The methods used to make coatings are physical vapour deposition (PVD) and chemical vapour deposition (CVD). The aim of this article has been to present an up to date review of the recent literature covering TiN preparation by both PVD and CVD method, as well as their characteristics and applications for various purposes. Without pretense to have covered the complete literature on the subject, it has been intended to compare parameters of the PVD and CVD preparation methods and dependance of the TiN characteristics on them. It has been equally intended to determine the range of applications and relative suitability of the methods reviewed.

It has become evident that physical vapour deposition of TiN in the strict sense of the definition almost does not exist. The high melting point of TiN makes conversion of the solid compound into vapour if not impossible, then certainly very difficult and uneconomical.

The modified PVD methods therefore developed for the TiN preparation, termed in this article as "reactive PVD" correspond, in fact, to the definition of the CVD. Nevertheless they were classified under PVD because they were born from the PVD methods and use the conventional PVD equipment with the necessary modifications.

However, the recently developed "plasma-assisted CVD" was treated separately primarily because it makes use of the conventional PVD equipment, but with the reactive gas mixture as in the conventional CVD.

2. TiN COATINGS PREPARED BY PVD METHODS

2.1. Short summary of PVD methods

In Physical vapour deposition (PVD) coatings are produced on solid surfaces by condensation of elements or compounds from the vapour phase, whereby the deposit has identical composition as the vapour.

PVD procedures can be differentiated into three groups:

- Evaporation
- Sputtering
- Ion plating

2.1.1 Evaporation. In the evaporation process, vapours are produced from a material located in a source which is heated by different ways. For high melting point materials electron beam sources are usually employed. The process is usually carried out in vacuum 10^{-5} to 10^{-6} mbar. The substrate is usually at ground potential and may be heated to several hundred degrees. Figure 2.1 is a scheme of a vacuum evaporation system using electron beam heating.

Evaporation processes for the deposition are further subdivided into two types: a) direct evaporation, b) reactive evaporation.

In direct evaporation the evaporant is the same as the coating. It is used to produce metal coatings or coatings of lower melting point compounds.

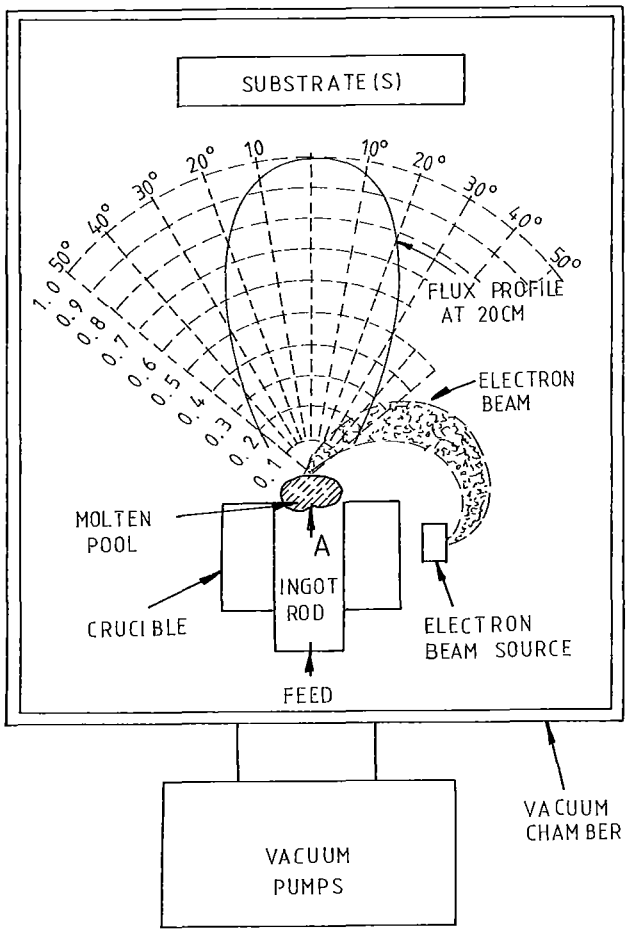

Fig. 2.1. Vacuum-evaporation process using electron-beam heating (Bunshah 1988).

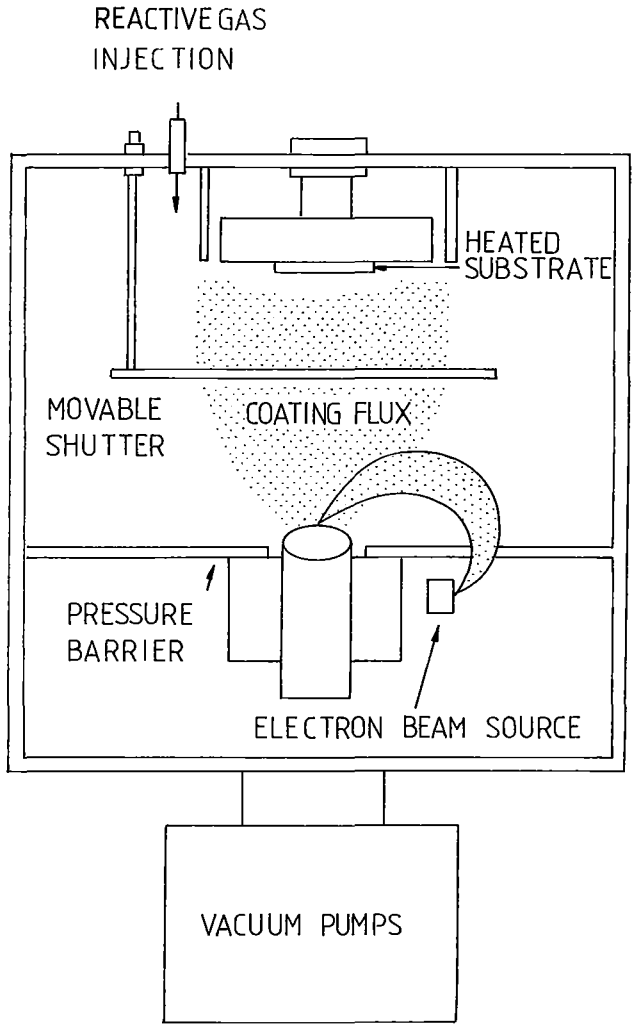

Fig.2.2. Reactive evaporation
(schematic)

For making coatings of high meting point compounds, the reactive evaporation must be used. In the reactive evaporation metal vapours are produced in the presence of a partial pressure of the reactive gas to form a compound either in gas phase or on the substrate as a result of a reaction between the metal vapour and the gas atoms, e.g.:

$2Ti + N_2 \rightarrow 2\ TiN$

The fig. 2.2 is a scheme of the reactive evaporation system.

To gain higher coating rates, the reaction gas can be activated by means of an electric glow discharge (activated reactive evaporation - ARE).

The evaporation unit must be extended by an additional electrode between the substrate and the source (fig.2.3).This electrode has a positive potential and an accelerating voltage of several hundred volts which pulls the electrons from the plasma above the melting pot to the reaction zone. These electrons activate the metal vapour and the reactive gas, which leads to a raise in yield and therefore also in coating rate.

2.1.2. Sputtering. Sputtering is the emission of material particles from solid surfaces (targets) which are bombarded with high energy particles, usually Ar gas ions. The process takes place in vacuum chamber in which the electrically insulated cathode (target), being the negative electrode, and the substrate carrier, serving the purpose of an anode, are present (fig.2.4.).

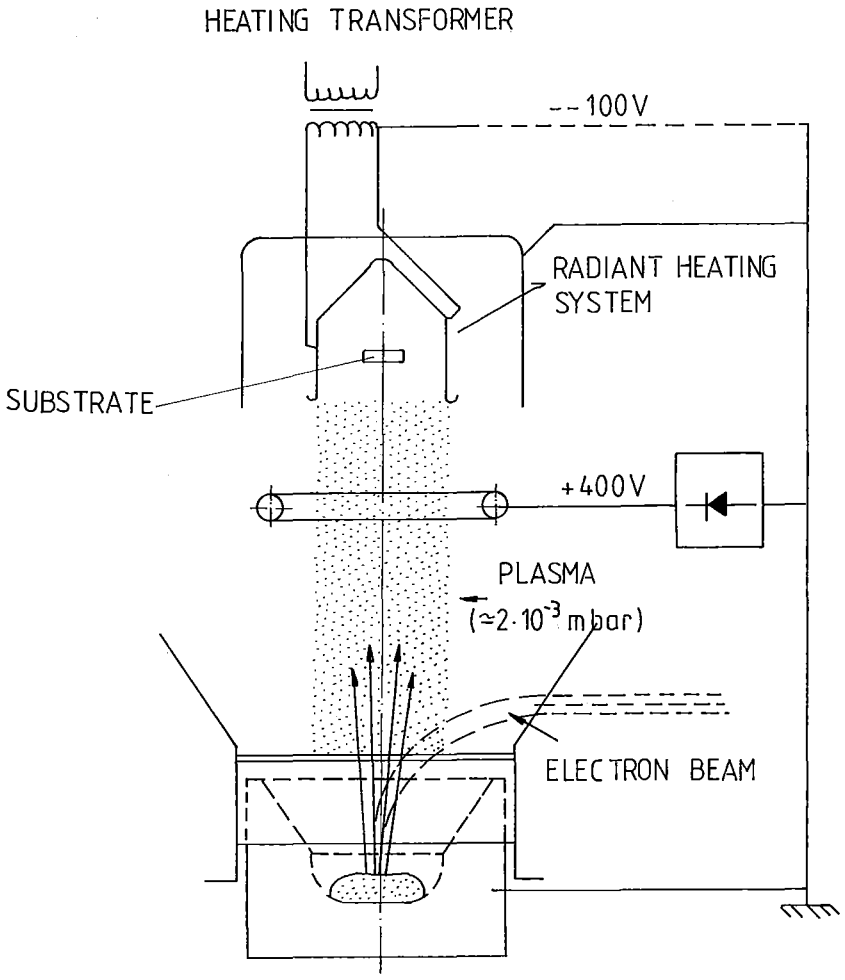

Fig. 2.3. Activated reactive evaporation (ARE) (schematic) (Lugscheider 1981).

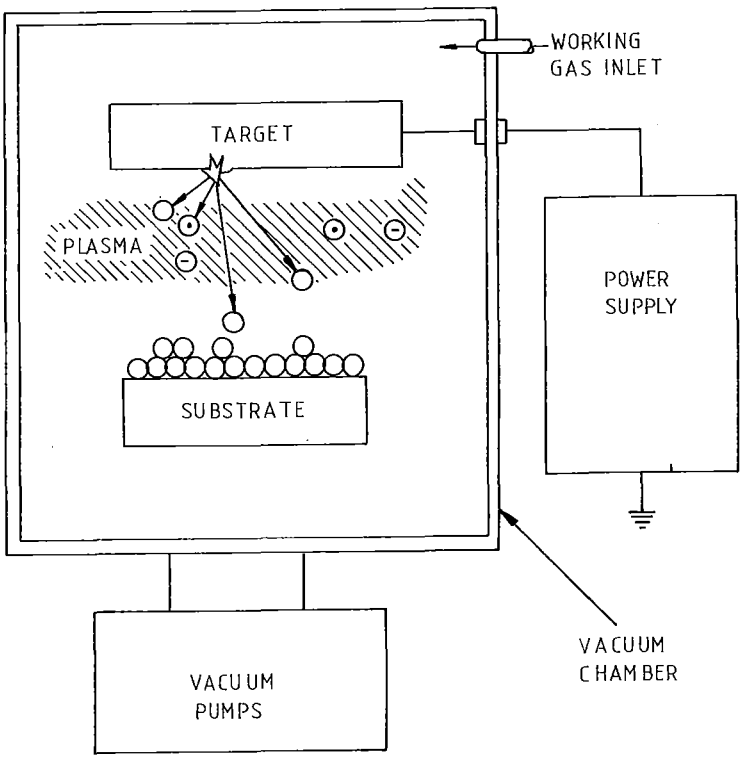

Fig. 2.4. Basic sputtering process (Bunshah 1980).

The plasma located between the electrodes consists of neutral particles, ions and free electrons, and is therefore electrically conductive.

The diode arrangement may be either a direct voltage sputtering (dc), or high frequency (or radio frequency-rf) voltage sputtering. The d.c. sputtering is used for metals and the r.f. sputtering is used both for metal and dielectric target materials.

A further modern variant makes use of magnetron sputtering. In this case the electronic alternating field is superposed by additional magnetic field (permanent magnet, electromagnet). This arrangement provides an order of magnitude increase in deposition rate over that of planar diodes.
It also can provide uniform deposition over very large substrate areas (many m^2).

The substrate can be on a low negative potential. This arrangement is so-called bias-cathode sputtering. This enhances the adhesion and the density of the coatings.

Reactive sputtering is a method of cathode sputtering in which the plasma fulfils two functions. The first is to maintain the actual sputtering. The second role is to carry the reactive components (gases) which are meant to react chemically with the target material. This method is applicable when coating has to be compound. In this case a metal target is sputtered in a mixture of Ar and a reactive gas (e.g. Ti target and N_2 gas produce TiN coating).

2.1.3. Ion plating. The most modern of the three PVD method is ion plating. This method was born from the desire to make optimal use of the advantages offered by the other two PVD method - the high coating rates of the high-vacuum evaporation and the good surface adhesion gained by cathodic sputtering.

Contrary to the sputtering method, in the ion plating the surface to be coated is exposed to ion bombardment before and during deposition. The material to be evaporated is ionized only in a small amount (<1%); nevertheless, due to the acceleration in the electric field the particles are loaded with such a high amount of kinetic energy that, depending on their specific mass, they penetrate more or less deeply into the substrate and are deposited in zones close to the surface (ion implantation). Scheme of an ion plating unit is presented in fig.2.5. The advantages of ion plating are good adhesion and coating rates comparable to those of evaporation.

Reactive ion plating (RIP) is very similar to the reactive evaporation process in that metal atoms and reactive gases react to form a compound, aided by the presence of a plasma. Since the partial pressures of gases in reactive ion plating are much higher ($>10^{-2}$ mbar) than in the ARE process (10^{-4} mbar), the deposits can become porous or sooty.

2.2. Preparation of TiN coatings by PVD methods

2.2.1. Preparation of TiN coatings by evaporation. Due to a high melting point, TiN coatings can not be produced by simple evaporation of TiN. Instead,reactive evaporation methods are used, in which Ti metal is evaporated in an N_2 atmosphere and sufficient energy is provided that the components can react to form TiN.

Ting (1982) used a conventional evaporator in which Ti was evaporated from a resistance-heated tungsten boat in a N_2 atmosphere at a low pressure ($pN_2 = 10^{-5}$ bar). The deposition was effected into a cool substrate. In order to make reaction between Ti and N_2, the substrate was annealed at 700-900^{o}C. The TiN formation was confirmed by X-ray diffraction.

The TiN coating is more easily produced if for evaporation of Ti an electron beam gun is employed and simultaneous bombardment by N_2 with an energy of 10-30 keV is done (Satou, 1985).

To gain higher efficiency the reaction gas can be activited by means of an electric glow discharge (activated reactive evaporation-ARE process). For this purpose a standard evaporation unit with an electron beam gun, extended by an additional electrode was used. Ti was evaporated in N_2 at a pressure of 2.1 -3.4 bar. The substrate was at ground potential (Kaufer 1978, Jacobson 1979, Jamal 1980, Wendler 1986), or at a negative bias potential (Hahn 1987). A dc power supply was used to provide the ARE discharge and substrate bias.

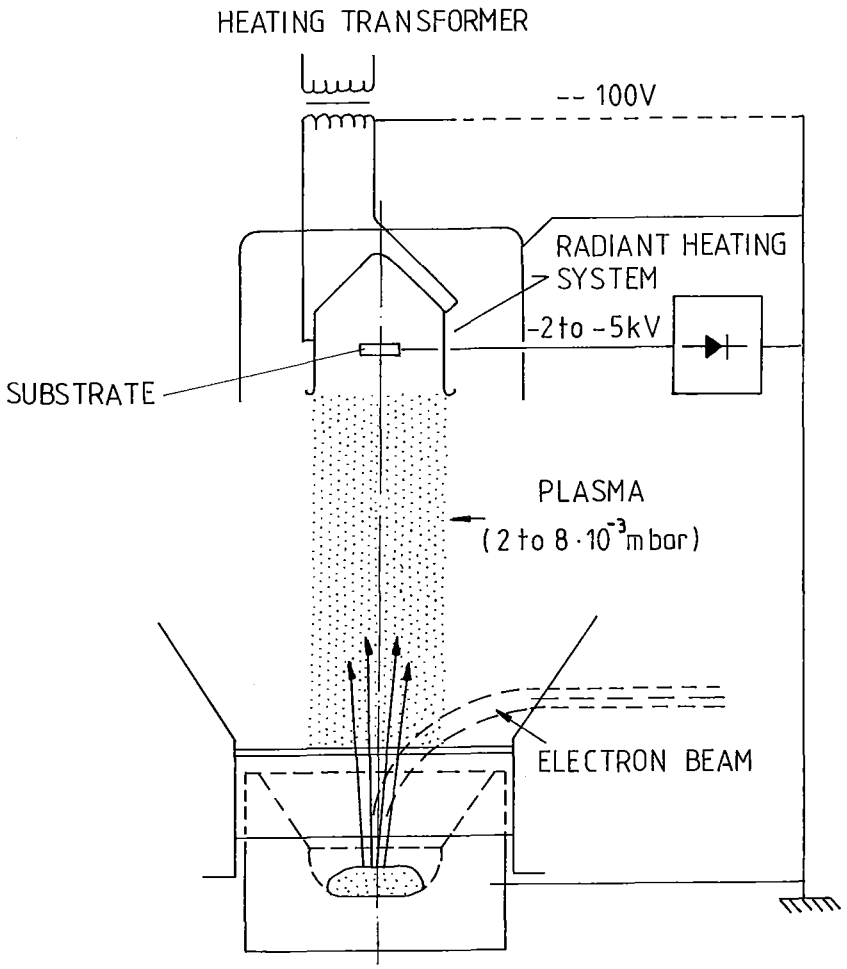

Fig. 2.5. Scheme of an ion plating unit (Lugscheider 1981)

To produce TiN films at near-ambient temperature, an ion-stimulated sorpion process was used (Martev 1985). Titanium was sublimated by electron bombardment heating in a magnetic field. The electrons were emitted from a hot filament and served both for heating the Ti-anode and gas ionization. The method is applicable when low temperature is necessary. The ion-stimulated sorpion process provides an advantageous alternative solution, because its effect is the same as the increase of substrate temperature.

2.2.2. Preparation of TiN coatings by sputtering. TiN coatings have been deposited by sputtering from a TiN target in the convetional triode sputtering system. Before the sputtering the system is pumped down to 10^{-7} bar. The substrate is before sputtering heated by electron bombardment for 45 min. Typical sputtering parameters are shown in Table 2.1.

Table 2.1.
Sputtering parameters (Mah 1974)

Target power (kV)	Argon pressure (bar)	Sputtering time (h)	Deposition rate (m/h)
1	$2 * 10^{-6}$	1.5	3

Because of high melting point of TiN, sputtering from TiN target is little used for TiN coatings preparation. The method mostly used is the reactive sputtering from a Ti-target in a nitrogen flow. For the purpose have been used either standard sputter coaters (Münz 1982a, Sproul 1983, Sundgren 1983 a,b,c, Wittmer 1982), planar magnetron sputtering systems (Cheung 1981, Je 1986, Valvoda 1986, 1988),or their modifications (Ahn 1983, Münz 1982 b).

A commercial sputter system was used for reactive sputtering from Ti-target in a N_2 + Ar gas mixture. With Ti target ϕ 5 cm and power of 150 W, deposition rate was 5 nm/min (Marinkovic 1974 b). With a ϕ 15 cm target and 1 kW deposition rate was higher (15 nm/min) (Hibbs 1983). The substrate was either at ground potential (Marinkovic 1974 b, Sundgren 1983 a,b, Hibbs 1983, Wittmer 1982), or at negative bias potential (Sundgren 1983 c, Yamashina 1983).

The substrate can be mounted on a cylindrical substrate carrier which rotates during the deposition (Münz 1982 a). Such a modification gives a uniform coating thickness. A very high deposition rate, 1.8 mm/h, can be obtained by reactive sputtering from Ti-target with 10 kW power in a N_2 + Ar mixture at 10 mbar (Sproul 1983).

A standard magnetron sputtering unit can also be used for TiN preparation. A Ti target is sputtered in a N_2 + Ar mixture at $9*10^{-6}$ bar (Valvoda 1987, 1988) or 90 mbar (Cheung 1981).During the sputtering the substrate is either unheated (Je 1986), or heated to 50-150^{o}C (Valvoda 1987, 1988).

A variant of reactive sputtering makes use of the sputter gun. The sputtering system equipped with three Varian-S-guns was used (Ahn 1983). The substrate to gun distance was 20 cm and the substrate was at a bias potential of -100 V. During the operation the substrate temperature of 60-70^{o}C was reached.

A high rate sputtering process for preparation of TiN coatings can be used. Two pairs of cathodes, each 1.6 m long and 23 cm wide, permit the coating of 100-200 drills or end mills, mounted in a frame of dimension 1.2 * 0.6 m. The distance between the cathodes was up to 20 cm (Münz 1982).

2.2.3. Preparation of TiN coatings by ion plating. By reactive ion plating TiN coatings can be prepared on industrial tools weighing over 20 kg (Matthews 1980), or on cemented carbide tools (Perry 1987).

The reactive ion plating method is used for industrial production of TiN coatings on cutting tools, twist drills and wrist bracelets (Buhl 1981).

A variant of reactive ion plating using the hollow cathode discharge (HCD) was also used for TiN coating preparation. It is characterized by a large flux of metal ions and by energetic particle bombardment of the substrate (Sato 1978)

The TiN "Balinit" coatings are commercially deposited on a variety of tools using an ion plating process (Balzers 1988). Titanium is evaporated in a vacuum chamber at a temperature below 500^{o}C and N_2 is simultaneously admitted.

2.3. Characteristics of TiN coatings prepared by PVD method

Characteristics of the TiN coatings strongly depend of their preparation.

Colour

The colour patterns of TiN changes from silver colour of pure Ti to the golden yellow colour for stoichiometric TiN, and to brown and then to dark rose for TiN films sputtered with high nitrogen partial pressures.

Thickness

Depending on the applied conditions TiN layers with thicknesses ranging from <1 μm up to 40 μm can be prepared by PVD method.

The layer thickness depends on the rate and time of deposition, the deposition rate depending on the power applied to the electron beam gun or target. Sputtering from a TiN target gives a relatively low deposition rate and therefore low thickness, while the reactive sputtering gives higher deposition rates and greater thickness. Reactive evaporation gives a relatively high deposition rate which can be increased by activation using an additional plasma.

Negative substrate bias produces lower deposition rate, because sputtering under these conditions leads to a removal of particles from the deposition layer.

Uniformity of layer thickness depends on the substrate-target distance. It can be achieved by rotating the substrate holder, but in this case a longer sputtering time is needed to obtain a given thickness than by the stationary sputtering.

Crystal structure

The TiN layers obtained by the PVD methods are polycrystalline, strongly (220) and/or (111) preferentially oriented.

At substrate temperatures below 500°C it is (111) (Hahn 1987). If a negative bias potential is applied to the substrate heated to 520°C, the intensity ratio I (200)/ I (111) increases with increasing bias potential up to a maximum situated at -600 V. Further increase of the substrate bias up to -1300 V leads to a decrease of the intensity ratio (Hahn 1987).

The lattice parameter of TiN films depends on their composition, but it remains equal to, or becomes greater than that of the bulk TiN.

Composition

The composition of the TiN coatings depends on conditions of their preparation. The films deposited at near-ambient temperature consist of δ-TiN and Ti-N. By annealing they are transformed into TiN (Martev 1985).The films deposited at 500°C consist of a two phase mixture of Ti_2N and Ti_xN_y, stable up to about 1000°C and 1100°C, respectivelly. Vacuum anealing over 1100°C leads to formation of stable δ-TiN in place of both (Wendler 1986).

Microstructure

The grain size of TiN layers, as reported by different authors, ranges from 5 to 150 nm. The wide range is presumably a consequence of different preparetion conditions of TiN coatings. It has been shown (Marinkovic 1972, 1974 a), that grain size of thin film increases with increasing deposition rate, substrate temperature and film thickness. This is expected to be also valid for the TiN films, so that the reported literature data might be commented on in this light.

According to Ahn (1983), the TiN layers 300 nm thick, deposited at 60-70^{o}C and substrate bias of -100 V had the grain size between 5 and 20 nm. Valvoda (1987) reported grain size values from 20 to 70 nm for the TiN layers deposited also at low temperature (50^{o}C), but the film thickness was greater in this case and therefore the grain size was greater too. Hibbs (1983) obtained grain size of 150 nm for the TiN films 5 μm thick, deposited at 475^{o}C. The grain size is greater because of higher deposition temperature. Jacobson (1979) found that grain size of the TiN layers increased with temperature. With other conditions identical, the TiN layers deposited with a substrate bias of -300 V had grain size half of that obtained without the bias (Sundgren 1985). The explanation may be based on the fact that the substrate bias reduces the layer thickness of the films deposited for a given time, the grain size being smaller because of the smaller thickness.

Adhesion

Adhesion of TiN coatings is influenced by the deposition temperature (Matthews 1985, Milic 1985). It can be measured by a pull test or using a scratch test

Pull test measurements show that adhesion is better when the layers are deposited at higher substrate temperatures. The adhesion values of TiN layres on tool steel vary from 2.02 MPa for room temperature deposition to 8.5 MPa for deposition at 200^{o}C. The highest adhesion, measued on dur-Al, was higher than 30 MPa (Milic 1985).

In the scratch test the samples were scratched with a rounded diamond stylus. The load was continuously increased from 0 to 100 N. The simultaneously recorded sound emission clearly indicated the "critical road", amounting for the TiN coatings from 10-18 N to $\simeq$ 30-40 N, for substrate temperature 25 and 475^{o}C, respectively (Kopacz 1985).

Microhardness

For microhardness of TiN layers a wide range of values has been reported by different authors, from below 10000 up to over 50000 MPa (Sproul 1983, Valvoda 1988, Jacobson 1979). Valvoda (1988) measured microhardness using 20 g load and obtained values extending up to over 50000 MPa. The unusually high values may be a consequence of the measuring method. Sproul (1983) made systematic microhardness measurements of TiN layers using different loads ranging from 15 to 200 g and measuring the indentations by means of optical microscopy and SEM. The microhardness values were found to be consideraly higher when smaller loads were applied, which might account for the high values obtained by Valvoda. The microhardness values of TiN layers from 23000 to 26000 MPa as obtained by Sproul could be taken as reliable, having in mind the mentioned detailed study. Similar microhardness values were obtained by Lin (1986) with loads of 50 and 100 g.

Microhardness of TiN coatings depends on their composition. The layers with stoichimetric composition have microhardness of about 22000MPa (Sundgren 1983 b).
With a decreasing N content of the layer, i.e. with an increasing content of the Ti_2N phase, microhardness is increased up to 26000 (Jacobson 1979), 28000 (Jamal 1980), 30000 (Münz 1982 a), or even 35000 MPa (Sundgren 1983 b)

The increasing substrate temperature was found to produce an increase in microhardness of TiN layers (Sundgren 1985). The increased substrate temperature can result in a decrease of the N/Ti ratio as a result of desorption of N_2 during growth, whereby Ti_2N phase content is increased.

Wear resistance

TiN protective layers extend life of coated tools. Life of the coated tool with respect to life of the uncoated tool is a measure of wear resistance.

Wear resistance depends on the nature of the substrate, tool shape and on whether one or both components of the pair are coated.

The coated end mill cutters outlasted their counterparts by a factor of 3.5 in milling the AISI 1035 steel, and they improved the surface finish of the cut. Uncoated end mill cutters produced a surface finish with an r.m.s. roughness of 2.5 μm, but this finish quickly deteriorated to a roughness of 4.1 - 5.1 μm. The TiN coated end mill cutters gave a surface finish with a roughness of 2.2 - 2.3 μm from start to finish (Sproul 1983)

The saw blades were used in a very difficult slitting operation. An AISI 1035 steel transmission brake band lined with friction material and joined together with a butt weld was slit into three parts with these blades, and the coated blades cut 2.2 times more bands than the uncoated blades (Sproul 1983)

The PVD TiN coating gave the same improvements to the WC tools as in the case of the CDV coatings (Mah 1973).

The TiN coated drill is able to make four times as many holes in a high strength steel as an otherwise identical uncoated drill (at the same cutting speed and feed rate) before regrinding becomes necessary (Buhl 1981).

Electrical resistivity

The variation in resistivity for thin TiN samples has been found to be wide and to depend critically on the growth conditions.

For dense and pure stoichiometric polycrystalline films resistivity values of about 25-30 μohm cm can be obtained, but two-phase films generally give values around 200 μohm cm.

Under otherwise identical conditions, the substrate bias influences electrical resistivity. Thus a -100 V bias produced the layer with a minimum resistivity value (~ 75 μohm cm), while without bias it was increased up to 300 μohm cm and with higher negative bias it was increased even to 500 μohm cm (Ahn 1987)

Optical properties

The TiN coatings have a high IR reflectance and an edge in the visible region. The maximum reflectivity varies between 0.75 and 0.95 at 20 μm, while the minimum one varies between 0.12 and 0.18 in the visible (Sundgren 1985, Ahn 1983).

2.4. Resume

Due to a high melting point of TiN, conventional PVD methods are unsuitable and generally are not used to produce TiN coatings. However, TiN coatings can be successfully produced by reactive PVD methods. Common to all reactive PVD methods is a chemical reaction between Ti vapour and N_2 gas.

Titanium vapour is generated by evaporation in electron-beam guns (reactive evaporation, activated reactive evaporation, ion plating), or from a Ti target (reactive sputtering).

The reaction takes place at low pressures (10^{-5} - 10^{-2} bar). Typical substrate temperature range is from ambient temperature to 300 - 400°C

The reactive PVD equipment is essentially the same as the conventional high-vacuum PVD units with minor modifications.

The deposition rate depends mostly on the applied power and varies from 3 to 50 μm/h.

Depending on the application, the coating thickness can vary from 0.2 - 0.3 to 10 μm.
The TiN composition depends on the conditions of preparation, the N/Ti ratio varying from above 1 to about 0.5.
The coatings are polycrystalline and preferentially oriented with (200) and/or (111) planes parallel to the deposition surface. The lattice parameter of the TiN layers is always greater than that of the bulk TiN.
The produced TiN coatings are typically compact, very hard, with extremely high wear resistance and good corrosion resistance. Microhardness values are typically in the range 22000 - 26000 MPa, i.e. higher than for the bulk TiN. The TiN coated tools can be used 2 to 4 times longer than those without coating. The layers adhere well to the substrate.
Their electrical resistivity varies from 20 to 500 μohm cm.
Their reflectivity is high in the far infrared (0.75 - 0.95 at 20 μm) and low in the visible.
Because of the low substrate temperature, the reactive PVD methods are suitable for all tools, including high-speed steel.

3. TIN COATINGS PREPARED BY CONVENTIONAL CVD METHODS

3.1. Short summary of CVD methods

Chemical vapour deposition (CVD) may be defined as the condensation of elements or compounds from the vapour state to form solid deposits, whereby the vapours have different composition from that of the deposit, the deposit being formed by chemical reactions which take place on or near the deposition surface.

As it was mentioned in the INTRODUCTION, in the section 2 on physical vapour deposition (PVD) have been included not only techniques of PVD in the strict sense, but also those developed from them (reactive PVD methods) which actually correspond to the definition of CVD. Therefore they will not be treated here.

In CVD the reactant gases, some or all of them generated by evaporation, are transported into the reactor containing a substrate, where they undergo a thermally activited chemical reaction. The solid products of the reaction are deposited on the substrate, while the by-product gases are removed from the reactor.

General considerations on the underlying thermodynamics and kinetics, evaporation, transport, nucleation and growth processes and tresses in the deposits are presented in the relevant books and monographs (Powell 1966, Gretz 1967, Jensen 1984).

Description of the CVD method

Typical CVD unit is in principle rather simple (fig. 3.1). It contains i) the part for providing the reactant gases, ii) the reactor and iii) part for the disposal of the by-product gases.

The first part usually contains the compressed gas bottles containing N_2, H_2, Ar, NH_3,CO_2 ect. Depending on the required purity of the product, the gases are used either as-supplied, or are additionally purified by passing through purifying units containing suitable chemical agents. The flow-rate of each gas has to be controlled by means of a suitable valve and measured using a flowmeter.

In addition to the compressed gas bottles, it is often necessary to have one or more additional reactant gases, most often halides of the elements that have to be deposited in the form of suitable solid product.
In order to be able to control the quantity of the halide introduced into the reaction chamber, the liquid halide is maintained at a constant temperature which determines its vapour pressure, and its vapour is carried by a controlled flow of a carrier gas (either reactant or neutral) which passes through the liquid halide thereby becoming saturated with its vapour before entering the reactor. In order to avoid premature reaction of the components, it may be necessary to introduce them separately into the reactor.

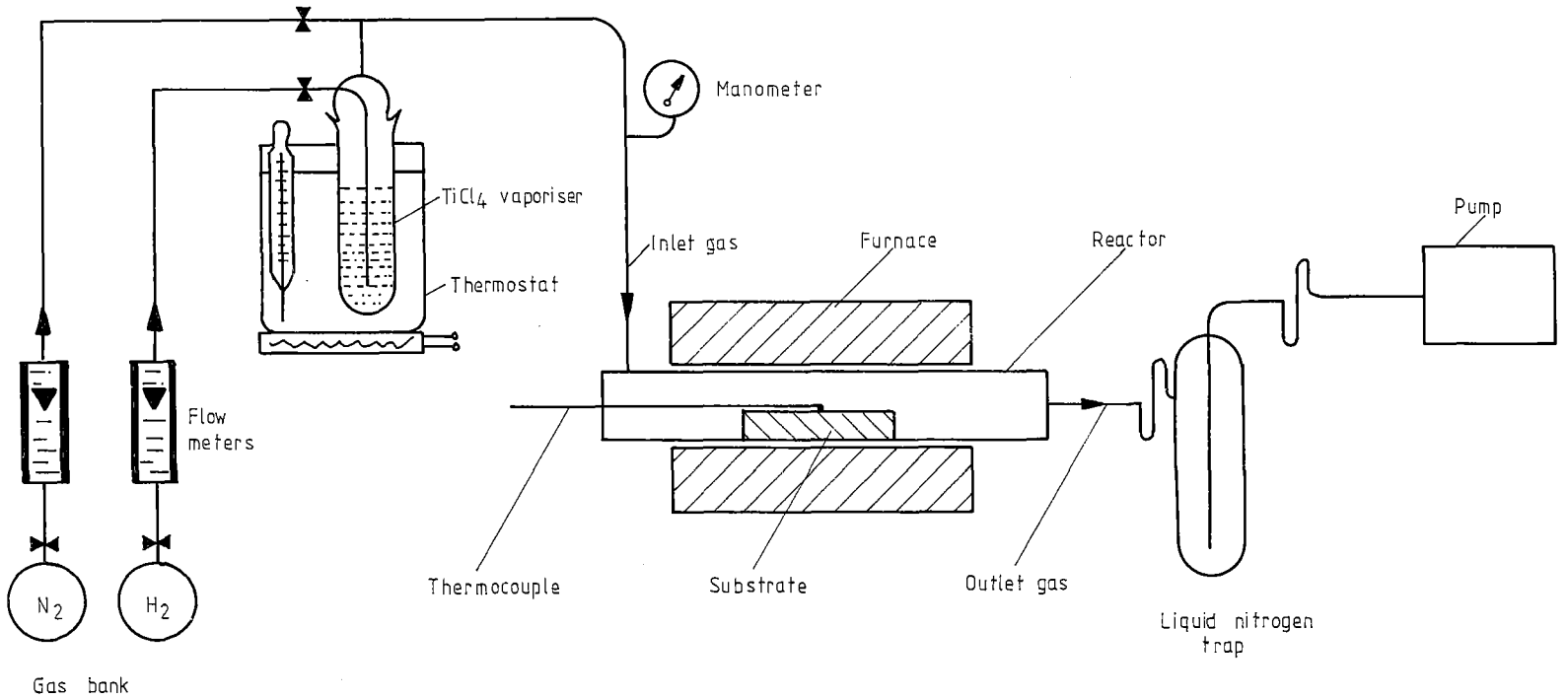

Fig. 3.1. Scheme of a CVD unit.

The role of the reactor, the type of which can be chosen depending on the necessary experimental conditions (Jensen 1984), is to provide favourable conditions for the chemical reactions and for deposition of the product on the substrate. The reacting components which are consumed by the chemical reactions are constantly supplied by a gas flow of the component gases. A suitable pump is employed for the purpose, especially if the process requires a reduced pressure.

Since in the conventional CVD process the chemical reactions leading to formation of the deposit are usually endothermic and the necessary energy is supplied by heating, the reactor must be heated either by a (resistance) furnace ("hot wall method") or by induction. In the latter case the substrate is heated either directly or from a separable susceptor ("cold wall method").

The reaction chamber (reactor) in which the chemical reactions and the deposition of the product on the substrate have to be effected must satisfy requirements which are derived from the process parameters (high temperature, corrosive gases, maintenance of the necessary flow-rate and total gas pressure ect).

The conditions in the reactor should be chosen so as to favour the chemical reaction. A good guide to a porper choice of the experimental conditions can be Gibbs free energy of given reaction which has to be negative. On the other hand, it is often necessary to look for a compromise which sacrifices to some extent the properties of the deposit on the account of reaching a reasonnable rate of deposition and cost of the material produced.

The by- product gases can be, depending on their nature and amount, let into the ventilation system and open atmosphere directly, or after having them chemically treated in situ, or accumulated at the end of the CVD apparatus using suitable trap(s), for subsequent treatement.

3.2. Preparation of TiN coatings by conventional CVD methods

CVD is a suitable method for TiN preparation. A volatile halide of Ti and not too high temperature at which its reaction with N_2 + H_2 or with NH_3 to produce TiN becomes thermodynamically favourable make this method a rather attractive one. Two chemical reactions, both employing $TiCl_4$ and atmospheric pressure have been used for TiN preparation (Table 3.1).

The reaction

$TiCl_4 + 1/2\ N_2 + 2\ H_2 \text{ ----> } TiN + 4\ HCl$ (1)

has been mostly used. From the dependance of the Gibbs free energy on temperature, presented in Fig 3.2 (Archer 1981), it follows that the reaction becomes thermodynamically favourable at 630^{o}C (900 K). However, temperatures employed for TiN preparation using this reaction (Table 3.1) were usually considerably higher in order to have a reasonably high deposition rate.

Since most of the articles dealing with CVD of TiN aim at establishing variation in deposition rate and TiN properties on experimental conditions, a wide range of variables has been employed. Thus temperature was varied from 700 to 1400^{o}C (in one article even up to 2200^{o}C), $TiCl_4$ content from 0.3 to 42 vol%, while partial pressures (volume contents) of N_2 and H_2 were varied in a very wide range. However, not all of the articles contain complete data concerning experimental conditions. Nevertheless, on the basis of the existing data it seems that temperature range chosen by a majority of the authors would be between 1000 and 1150^{o}C and the $TiCl_4$ concentration would be from a few percent to about 10 vol%. It is more difficult to be definite regarding partial pressures of H_2 and N_2; the ratio of 1 or above could be possibly chosen. As the carrier gas (carrying the $TiCl_4$ vapour), hydrogen, nitrogen or their mixture were used.

Table 3.1:: Preparation conditions, characteristics and applications of TiN coatings prepared by CVD* $TiCl_4 + N_2 + N_2$

Author, year	Preparation conditions	Appaparatus, substrate	Characteristics	Applications
Synielnikowa 1971	700-2000°C; $TiCl_4/N_2$ =0.5; 1; $N_2:H_2$=2.5, 1.5, 10. Optimum $H_2:N_2$=2.5, Ti/N_2=0.5	Grahite rod (or W) heated by Joule effect	700-1200°: golden, N/Ti=0.91, c= 0.424 nm; >1300°: brown, graphite reacts; higher T (W-subs.): golden, c=0.423-0.424 nm, N/Ti= 0.982-0.991. Cr.size incr. with T, cr. form does not depend on T. MH=15500.	No data
Peterson 1974	1000-1080°C; 2-30% $TiCl_4$	Hot wall vertical furnace, cemented carbide subs.	Low $TiCl_4$: high rate, columnar grains; med. $TiCl_4$: random str.; 30% $TiCl_4$: deposition stops.	Wear Resitance improvement
Takahashi 1974	700-1200°C; $N_2/TiCl_4$ =0-10	Hot wall vertical furnace. Graphite substrate.	R incr. with T and $N_2/TiCl_4$. R const. for $N_2/TiCl_4$>6. For $N_2/TiCl_4$=8 at 1200°C, R=8.1 µm /h. η(220) and cr. size incr. with T and $N_2/TiCl_4$. Whiskers can be produced.	
Kato 1975	110-1400°C; 0.3-42 % $TiCl_4$, 10-89% H_2, 3-89% N_2. τ=350 s.	Hot wall, horiz., graphite plate	T not uniform. $TiCl_4$ consumed before max T. $R \sim p_{H2}1/2$. $R_{max} \cong$ 1.1 mm/h. $TiN_{1.01}$ golden-yel., $TiN_{1.04}$ red-brown. c decr. with N/Ti.	
Schintlemeister 1976	915°C; 200 l/h H_2 satur. with $TiCl_4$ at 37° (26 mbar). 85-105 min. H_2/N_2=1.	No data, cemented carbide subs.	$R \cong 0.1$ µm/h. Ni incorp. into coating. Rupture strength of subs. reduced by coating.	Wear resistance improvement. Decorative effects.

Author, year	Preparation conditions	Appaparatus, substrate	Characteristics	Applications
Takahashi 1977	700-1150°C, H_2 satur. with $TiCl_4$ at 70° (130mbar). 7.4-8.7% $TiCl_4$, 55-72% H_2, 19-37% N_2). Ultrasonic source applied to subs.	Cold wall vertical, low carbon steel subs.	R≅0 at <900°; incr. with T. R=3 µm/h at 1100°, η(220). Adherent film only with ultrason. Hard films.	
Politis 1979	1600-2200°C; H_2+N_2 (1:1) satur. with $TiCl_4$ at 0-23° (2.6-13 mbar). $N_2/TiCl_4$ 40. τ=14-37s.	Cold wall horiz., Mo-tube subs.	Single cristals. Pref. shape cube. (100) most often. N/Ti from 0.935 to 1.002, most often 0.98. c has a max of 0.42409 nm at N/Ti ≅0.96. Supercond. at 5.8-6.2 K.	
Kim 1983	1050°C, H_2; satur. with $TiCl_4$ at 50° (56 mbar). 3% $TiCl_4$, H_2=N_2=48.5%. τ from 0.5 to 10s.	Hot wall horiz., cemented WC coated with TiC subs.	Growth along (220) plane. Cr. size incr. with T, decr. with P_{TiCL_4}, incr. with total flow rate up to 42 1/h, then const.	Improvement of properties of cemented WC cutting tools using double TiC/TiN layer coating.
Mantyla 1985	980°C, 1-3.5% $TiCl_4$ 56.5-63% H_2, 36-40% N_2	Hot wall, chrom. tool steel subs.	Very dense coating, (220). Very good corr. resist., controlled by coating defects.	
Jung 1986	900-1200°C, H_2 satur. with $TiCl_4$. Optimum: 1000°, 0.8% $TiCl_4$, N_2/H_2=1/2, 72 1/h total flow rate	Hot wall vertical, low-carbon steel sub.	No data	

Author, year	Preparation conditions	Appaparatus, substrate	Characteristics	Applications
Itoh 1986	1050°C, H_2 satur. with $TiCl_4$ at 30-70°(40-130 mbar). 0.5% $TiCl_4$, H_2/N_2=1.	Hot wall horiz. Furnace moving along steel tube subs.	Compact film with uniform thickness distrib. η(220). Excellent corr. resist.	Improvement of corr. resistance
Motojima 1986	800-1100°C; flow-rates: 9 l/h H_2, 3.35 Ar, 1.48 N_2+ $TiCl_4$. $N_2/TiCl_4$ from 1 to 16.	Steel subs., also Cu,Ni.	Corr. resist. is better for low-T coating (<1000°). Extreme wear. resist., increasing with T up to 950°, then decrease	Corr. and abrasion protection of steel (sea water and whirled sand).
Lhermitte Sebire 1986	1100°C, no data	Cemented carbide subs.	Thick (40 μm layer with well-developed columnar microstr. Strong adherence with Al_2O_3 layer depos. onto it.	Improvement of wear resist. of cutting tools by TiN+Al_2O_3 double layers.
Tsao 1987	N_2 satur. with $TiCl_4$. Mixed with H_2 just before reactor.	Hot wall, vertical low-carbon steel subs.	No data	
Telema 1987	1000°C; 0.5-3%$TiCl_4$, 15-60%N_2. Linear gas flow velocity 1.2 - 2.8 m/min.	Hot wall, Ni-based and Fe-based alloy subs.	Effect of subs. on growth rate. Liquid Cr and Fe chlorides formed, caused interlayer porosity of Fe-alloy subs.	

Author, year	Preparation conditions	Appaparatus, substrate	Characteristics	Applications
$TiCl_4 + NH_3$				
Saeki 1982	700-1400°C, Ar satur. with $TiCl_4$ at 105°(>300 mbar). 2.9%$TiCl_4$, NH_3=Ar= 48.5%.	Transp. quartz or Al_2O_3 tube subs.	When incr. from 700 to 1000-1400°, N/Ti decr. from 1.21 to 1.10 and c incr. from 0.4224 to 0.4233 nm.	
Kurtz 1986	400-700°C; He or Ar satur. with $TiCl_4$. 0.01-10% $TiCl_4$, 0.1 -15% NH_3. Linear gas flow velocity 54-84 m/min	Hot wall, horiz., spec. injector to mix uniformly gases. Corning glass or Si-wafer subs.	Thickness <0.1 to >0.5 µm. Good adherence if <0.05 µm. Hardness 8.5 (Mohs). Deposition rate 27 and 360 µm/h at 600 and 650°, resp.	- Heat mirrors for summer architect applications; - Very hard protective coatings.

* Ambient pressure was used in alle cases. c is the lattice constant.
R stands for deposition rate and η for preferred orientation. MH is microhardness, τ is residence time.
Abbreviations: cr.=crystal, subs.=substrate, incr.=increase, decr.=decrease, const.=constant, horiz.= horizontal corr.=corrosion, resist.=resistance, satur.=saturated, yel.=yellow, pref.=preferred, cond.=conductive, spec.=special resp.=respectively, distrib.=distribution, str.=structure

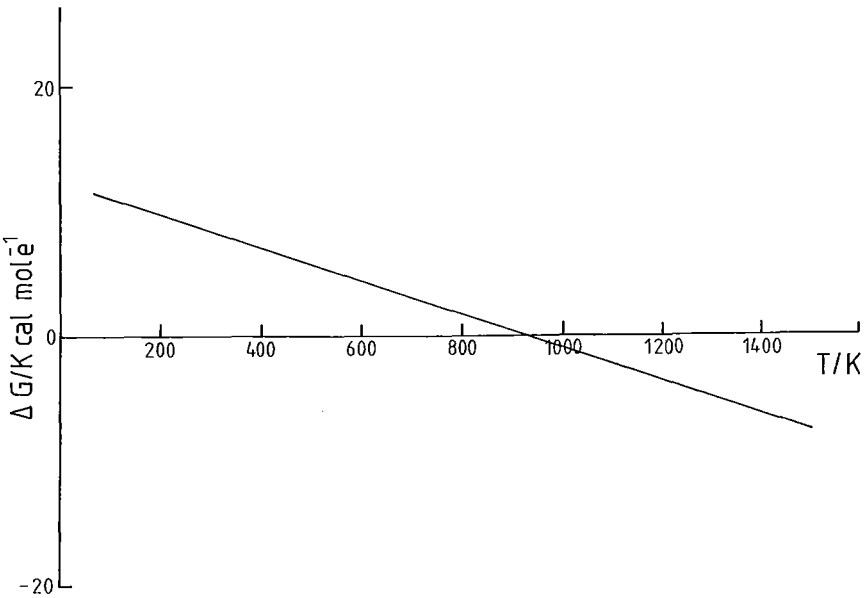

Fig. 3.2. Free energy of formation of TiN.
(Archer 1981)

The value of contact or residence time (interval of time during which the gas mixture is in the contact with the substrate) are usually not given.
The data concerning (total) flow rate which are rather often presented, are not suitable for comparison because of a variety of dimensions of the working space used by different authors. Still the data presented in some of the articles make possible to calculate more or less accurately the residence time. It follows that residence times used vary in a wide range, from a few seconds to about 6 minutes,

Concerning the deposition rate, again only some of the articles give the value obtained. Generally the deposition rate increases with increasing deposition temperature. Takahashi (1974) found that the deposition rate increased also with $N_2/TiCl_4$ mole ratio, but above $N_2/TiCl_4 = 6$ it became almost constant. According to Peterson (1974), the deposition rate is high at low p_{TiCl_4} and the depossition almost stops as p_{TiCl_4} was increased to 0.3 bar. Kato (1975) found that the deposition rate increased with p_{H_2} and obtained a maximum value of 1.1 mm/h.

In order to improve uniformness of the deposit thickness along a steel tube, Itoh (1986) used a furnace which moved by a constant speed along the tube. A very uniform thickness distribution was achieved. Takahashi (1977) applied ultrasound to a low-carbon steel substrate in order to achieve a good adherence of the deposit. Problem of adhesion of TiN coating and steel substrate was also studied by Lhermitte-Sebire (1986) and Motojima (1986) who reported that a better adhesion had been obtained at higher deposition temperature, as it should be expected. The latter authors have also studied corrosion resistance in sea water and abrasion resistance to whirled sea sand. The fine grained smooth TiN layers obtained at low temperature had higher corrosion resistance, probably because there was less defects - pinholes and craks in the deposits obtained under such conditions. Abrasion resistance was found to be extremely high, with a maximum at 950^{o}C.

Corrosion resistance of steels coated by TiN layers was also investigated by Mantyla (1985). Both researchers found an excellent corrosion resistance which was ascribed to formation of a very dense and compact TiN coating, although Mantyla et al have stated that on larger surface areas some dangerous defects in the coatings might exist.

In the case of Ni-based and Fe-based alloys, Telama (1987) found that the substrate had an influence on the TiN growth rate, which for the two substrate differed by a factor 2. Chemical reactions were found to take place with the substrate, resulting of Fe and Cr chlorides.

Schintlmeister (1976) found an interaction between a cemented carbide substrate and the coating. The Ni from the substrate was incorporated into the coating

Physical properties of the deposits have been investigated by many researchers. Polycrystalline deposits with crystallite size increasing with temperature and $N_2/TiCl_4$ ratio (Takahashi 1974, Synielnikowa 1971, Kim 1983) are generally produced, the execption being the work of Politis (1979) who produced single cristals by working at high temperature.

The stoichiometry of the TiN coatings was investigated by Synielnikowa (1971), Kato (1975), and Politis (1979). Kato found that due to a premature consumption of $TiCl_4$, TiN_x deposits with x varying from 1.01 to 1.04 were produced. Both lattice constant and colour of the deposits were found to depend on the composition: the lattice constant decreased with N/Ti ratio and the colour was changed from golden yellow to red brown as the x value increased. In the work of Politis (1979) high temperature (1600 - 2200^{o}C) and $N_2/TiCl_4$ ratio 40 were used to prepare TiN single crystals on a molydbenum tube substrate. The crystals produced had x values ranging from 0.935 to 1.002. The lattice constants vs composition curve was found to present a maximum at N/Ti 0.96. Superconductivity of the crystal was found between 5.8 and 6.2 K.

In a number of articles (Takahashi 1974 and 1977, Kim 1983, Mantyla 1985, Itoh 1986) preferred orietation of the coatings was reported to exist, the (220) planes of TiN crystals being parallel to the substrate surface. In the work of Politis (1979), however, single crystals were grown most often with (100) preferred orientation.

Mechanical properties of the TiN coatings on a cemented carbide substrate were studied by Schintlmeister (1976), who found that rupture strength of the substrate was reduced by the coatings.

Synielnikowa (1971) reported microhardness value of 15500 MPa, and Takahashi (1974) found that microhardness of the deposited TiN layers was higher on their surface than on the cross-section, this being presumably a consequence of the preferred orientation.

The reaction

$$6\ TiCl_4 + 8\ NH_3 \text{ ---> } 6\ TiN + N_2 + 24\ HCl \quad (2)$$

has been used as an alternative method of TiN preparation by CVD, its most important advantage being lower deposition temperature. The reaction becomes thermodynamiically favourable above 300^{o}C, but does not give an appreciable film growth below 400 - 450^{o}C (Kurtz 1986).

In the work of Saeki et al (1982) temperature from 700 to 1400^{o}C was used, while Kurtz (1986) used a considerably lower temperature (400 - 700^{o}C). Ar or He used as carrier gases. Saeki used a gas mixture which contained 2.9 vol% $TiCl_4$ and equal concentrations of NH_3 and Ar, to deposit TiN on a transparent quartz or Al_2O_3 substrates. Kurtz used a wide range of composition (0.01 to 10 vol% $TiCl_4$, 0.1 to 15 NH_3) and a special nozzle to mix the gases uniformly in order to avoid powder production, the substrates being Si wafers or corning glass. Another difference between the two papers is in the residence time: 45 s (Saeki 1982) and a fraction of one second (Kurtz 1986).

According to the authors of the latter paper, their method of TiN coating preparation is suitable for mass production and has some advantages over other methods, including those in which organometallic compounds are used as starting materials. The advantages are the atmospheric pressure, lower temperature than that required if the reaction (1) is used, relatively wide temperature range, better adhesion of the films produced and starting reagents which are less expensive, less air sensitive and more volatile than the organometallic compounds.

Saeki reported the film composition rich in N, with x in TiN_x decreasing with increasing deposition temperature from 1.21 at 700^{o}C down to 1.10 at 1000 - 1400^{o}C. At the same time, the lattice constant increased from 4.224 to 4.233 A, this behaviour being in agreement with the already mentioned papers.

Kurtz prepared the films from about 0.1 to 0.5 μm thick, with a good adherence for the thicknesses below 0.05 μm. The hardness of the films is reported to be 8.5 on the Mohs scale. The films are typically 80 - 90 % reflective at IR wavelengths and about 20 % reflective to visible light, which roughly agrees with results of Synielnikowa (1971). The optical properties were found to depend on the working conditions and film thickness (Kurtz 1986).

3.3. Resume

TiN coatings can be successfully produced by conventional CVD method, using $TiCl_4$ - H_2 - N_2 or $TiCl_4$ - NH_3 mixtures at ambient pressure.

Typical working conditions with $TiCl_4$ - H_2 - N_2 mixture are: temperature 1000 - 1150^{o}C, partial pressure of $TiCl_4$ from a few vol% to about 10 vol%, H_2/N_2 ratio $\geq$ 1. By working with $TiCl_4$ - NH_3 mixture lower temperature can be used. The CVD apparatus therefore requires a high temperature furnace, but it can operate at ambient pressure.

The deposition rate depends on the working conditions and varies from a few micrometers to about 1 mm per hour.

The deposited TiN layers can have a rather wide range of composition, with N/Ti ratio from 0.93 to 1.21.

They are typically polycrystalline with (220) preferred orientation.The values of the parameter of crystal lattice depend on the composition, showing a maximum of 0.42409 nm an N/Ti 0.96. Using high deposition temperature ($\geq$1800^{o}C) single TiN crystals can be produced.

The TiN coatings are typically compact, very hard (8.5 on the Mohs scale), with extremely high wear resistance and good corrosion resistance. Corrosion resistance of the TiN layers is excellent, but that of the coated substrate depends on the defects in the coating.

Adherence of the layers is good at high temperature and for low coating thicknesses, but special techniques are needed to achieve reasonable adherence at lower temperature and for higher thickness.

The TiN layers have good electrical and thermal conductivity and show superconductivity at 5.8 - 6.2 K.

Reflectivity of the layers is 80 - 90% in the IR (for wavelenghts of about 20 m) and about 20% in the visible region.

Colour of the layers is golden-yellow at near-stoichiometric composition and changes to red-brown at higher N/Ti ratio.

Due to a relaively high temperature of the CVD process, its applicability for coating cemented carbide and steel cutting tools by TiN is difficult and is virtually impossible for high-speed tools.

4. TIN COATINGS PREPARED BY PLASMA ASSISTED CVD

In order to avoid negative effects of the excessive heating of substrates used as cutting tools during the process of CVD, various means have been tried. One of the possibilities examinated was to replace the N_2 - H_2 mixture in the CVD procedure by NH_3, which has enabled the researchers to work at considerably lower temperatures.

Another qualitatively different and more promissing approach consists in providing the energy necessary to activate the chemical reaction by using a dc or rf glow discharge. Ionization of the gases leads to a production of electrons and ions which are accelerated in the electric field thus increasing the number of high-energy inelastic collisions. The energy content of the species in the plasma can reach average values which correspond to much higher temperatures in a pure thermally activated process. In this way it is possible to maintain the reacting gases at high energy, keeping the substrate at a relatively low temperature.

Archer (1981) has described a plasma-assisted procedure in which a conventional dc sputtering unit has been used to deposit TiN from the $TiCl_4$ - N_2 - H_2 mixture as used in the conventional CVD procedure (fig.4.1), with addition of the plasma-sustaining argon gas. A nickel foil used as a liner to the surface of the cathode served as the substrate. The coating was deposited on the nickel foil at a pressure of 13 - 15 mbar. The coated foil was allowed to cool in hydrogen. The investigated substrate temperature range was from 250 to 600°C. Although the TiN coatings were obtained down to 250°C, their adherence to the substrate was poor below 400°C. The desposition rate of 1.0 μm/h at 600°C was about twice that of the run without plasma assistance.

Mayr (1986) produced TiN layers in a conventional dc plasma unit using the same gas mixture as in Archer's experiments. A temperature range from 430 to 700°C, 5 mbar total pressure and a constant Ar/N_2 ratio were used to deposit the coatings on a stainless steel substrate kept at a negative potential.

A TiN layer 5 - 6 μm thick, showing (200) and (220) preferred orientation, was obtained by working for 3h at 500°C. The composition of the coating was found to depend on pN_2 and substrate temperature, but stoichiometric TiN layers were deposited over a relatively wide range of these parameters (e.g. 500 - 700°C).

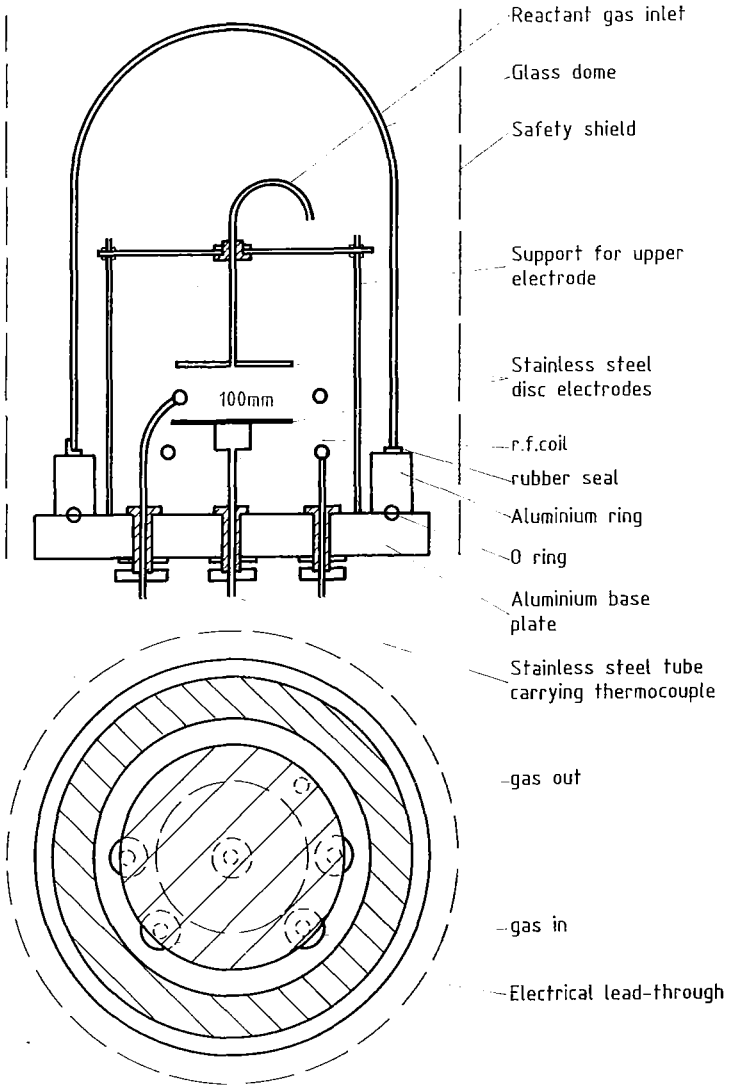

Fig. 4.1. Reaction vessel for plasma-assisted CVD.
(Archer 1981)

A systematic study of hardness as a function of TiN composition (Fig. 4.2) has shown that for the N/Ti ratio varying from about 0.8 to 1.1 there is an apparently linear decrease of hardness from about 35000 down to about 10000 MPa.

In order to avoid corrosion of the equipment, the authors tried to prepare TiN layers by replacing $TiCl_4$ with titanium-isopropoxide, $Ti(OC_3H_7)_4$. However, the coatings obtained in this procedure contained, in addition to Ti and N, also C and O atoms.

Kikuchi (1984) used similar experimental conditions to deposit TiN on high-speed steel and cemented carbide cutting tools. A systematic study was made in order to establish effect of process parameters on the properties of the coated substrates and effect of Cl- content in the coatings on their wear resistance.

An increase in substrate temperature above 500° C and negative voltage above 420 V were found to reduce hardness of the high-speed steel.

Interesting conclusions were reached with respect to Cl-content of the TiN coatings: the Cl-content is reduced when p_{TiCl_4} is lowered and substrate temperature increased. This is important because wear resistance is markedly reduced by Cl-content.

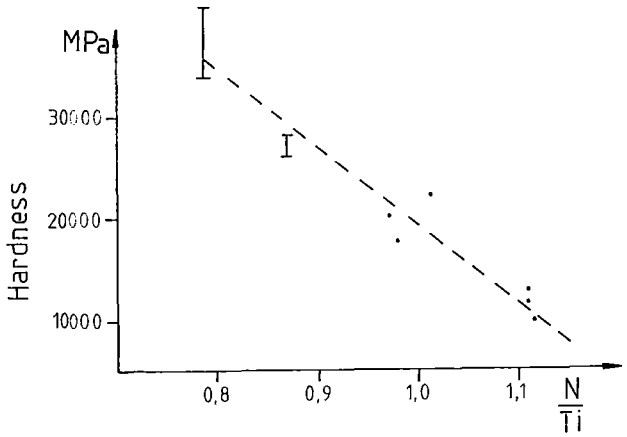

Fig.4.2. Relationship between hardness and N/Ti ratio (Mayr 1986).

The optimum working conditions (500°C, 1.3 mbar total pressure, 0.9 % $TiCl_4$, 6 % Ar, 62.5 % H_2 and 31 % N_2) resulting in a deposition rate of 60 μm/h, produce a highly wear resistant TiN layer and greatly improve cutting performance of both investigated substrates.

In conclusion it can be said that by employing plasma-assisted CVD (PACVD) the deposition temperature can be substantially lowered, so that the TiN layers having essentially the same properties as those produced in the conventional CVD can be produced at 400 - 500°C with a reasonable deposition rate.

5. APPLICATION OF TiN COATINGS

TiN layers are characterized by high hardness, chemical stability at elevated temperatures, excellent wear-, corrosion- and erosion-resistance, golden colour and high reflectivity in the infrared region combined with a relatively good transmission in the visible region.

Because of such characteristics, TiN layers are applied as protective coatings against abrasion, erosion and corrosion (Balzers 1988, Schintlmeister 1976, Motojima 1986), as diffusion barriers in silicon-device technology (Kanamori 1986, Gordon 1984) and for decorative purposes (Münz 1982 a, Schintlmeister 1976). Optical properties of TiN layers in the IR and visible regions have caused their investigation as solar energy absorbers and transparent heat mirrors (Kurtz 1986).

Table 5.1 contains requirements for TiN coating characteristics for their particular applications.

Table 5.1

Requirements for TiN-coating properties for various applications

Application / Property	Machining devices	Silicon devices	Decorative	Heat mirrors
Colour	not critical	not critical	golden-yellow	not critical
Thickness	5-20 μm	50-200 nm	2-5 μm	$\leqslant$ 100 nm
Grain size	Fine to coarse	very fine	very fine	very fine
Adhesion	High	High	High	High
Hardness	High	Not critical	High	High
Corrosion resistance	Good	Not critical	Very good	Good
Wear resistance	Good	Not critical	Good	Good
Electrical resistivity	Not critical	~ 500 μohm cm	Not critical	Not critical
Reflectivity in IR	Not critical	Not critical	Not critical	> 60 %

6. CONCLUSION

TiN coatings can be produced by the reactive PVD and CVD methods. The reactive PVD methods require high vacuum and low temperature, the corresponding equipment being relatively complicated and expensive.

The conventional CVD methods require simpler and less costly units for work at higher temperature and ambient pressure.

The recently developed plasma-assisted CVD method uses the equipment developed for PVD and reacting gas mixture as that in a conventional CVD procedure.

The range of TiN coating properties is more or less the same in both the reactive PVD and CVD methods.

For the conventional CVD methods are typical higher deposition rates and, consequently, possibility to produce thicker coatings. Due to relatively high temperatures, the conventional CVD methods are difficult of impossible to apply to lower temperature substrates, particularly for the high-speed steels. For such substrates the reactive PVD and plasma-assisted CVD are suitable.

The reactive PVD methods are equally suitable for the substrates which are sensitive to corrosive gases used in the CVD methods.

The conventional CVD methods are more suitable for high-temperature substrates insensitive to corrosive gases.

In summary, the reactive PVD methods can be used to produce TiN coatings for all today's applications and on any substrate; the range of applications of the conventional CVD methods is limited, but they are simpler and less costly.

Literature

Ahn K.Y., Wittmer M. and Ting C.Y., Thin Solid Films, 107(1983)45.

Archer N.J., Thin Solid Films, 80(1981)221.

Balzers Ltd., Vacuum News, april 1988.

Buhl R., Pulker H.K. and Moll E., Thin Solid Films, 80(1981)265.

Bunshah R.F., SAMPE Quarterly, october 1980.

Cheung N.W., Seefeld H. von and Nicolet M.-A., J.Appl. Phys., 52(1981)4297.

Gordon R.G. and Kurtz S.R., US Patent 4.485,265, 1984.

Gretz R.D. and Hirth J.P., in: Proc. CVD Conf., Schaffhauser A.C., ed., Gatlinburg, Tenn., USA 1967, p. 73.

Hahn B.H., Jun J.H. and Joo J.H., Thin Solid Films, 153(1987)115.

Hibbs M.K., Sundgren J.-E., Jacobson B.E. and Johansson B.-O., Thin Solid Films, 107(1983)149.

Itoh H., Kato K. and Sugiyama K., J. Mater. Sci., 21(1986)751.

Jacobson B.E., Nimmagadda R. and Bunshah R.F., Thin Solid Films, 63(1979)333.

Jamal T., Nimmagadda R. and Bunshah R.F., Thin Solid Films, 73(1980)245.

Je J.H., Gyarmati E. and Naumidis A., Thin Solid Films, 136(1986)57.

Jensen K.F., Proc. 9th Intern. CVD Conf., Robinson McD., van den Brekel C.H.J., Cullen G.W., Blocher J.M. and Rai-Choudhury P., eds., The Electrochem. Soc., Pennington, N.J., USA 1984, p.3.

Kanamori S., Thin Solid Films, 136(1986)195.

Kato A. and Tamari N., J. Cryst. Growth, 29(1975)55.

Kaufherr N., Fenske G.R., Busch D.E., Lin P., Deshpandey C. and Bunshah R.F., Thin Solid Films, 153(1987)149.

Kikuchi N. and Oosawa Y., Proc. 9th Intern. CVD Conf., Robinson McD., van den Brekel C.H.J., Cullen G.W., Blocher J.M. and Rai-Choudhury P., eds., The Electrochem. Soc., Pennington, N.J., USA 1984, p. 728.

Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd ed., Vol. 23, J. Wiley, 1983, p. 135.

Kopacz U. and Jehn H.A., Thin Solid Films, 126(1985)265.

Lhermitte-Sebire I., Calmet R., Naslain R., Desmaison J. and Gladel G., Thin Solid Films, 138(1986)221.

Lin P., Deshpandey C., Doerr H.J. and Bunshah R.F., J.Vac.Sci. Technol., 5(1987)2732.

Lugscheider E. and Reimann H., Surface coatings by means of physical evaporation procedure, Lehr und Forschungsgebiet Werkstoffwissenschaften Rhein-Westf. Techn. Hochschule, Aachen 1981.

Mah G., Nordin C.W. and Fuller J.F., J.Vac.Sci.Technol., 11(1974)371.

Mantyla T.A., Helevirta P.J., Lepisto T.T. and Siitonen P.T., Thin Solid Films, 126(1985)275.

Marinkovic Ž. and Simić V., Thin Solid Films, 13(1972)S19.

Marinkovic Ž. and Roy R., Thin Solid Films, 24(1974)355 (a).

Marinkovic Ž., (1974) unpublished data (b).

Martev I.N., Grigorev G.I., Petrov I.G. and Dynowska E., Thin Solid Films, 131(1985)303.

Matthews A. and Teer D.G., Thin Solid Films, 72(1980)54.

Matthews A. and Lefkow A.R., Thin Solid Films, 126(1985)283.

Milić M., Milosavljević M., Bibić N. and Nenadović T., Thin Solid Films, 126(1985)319.

Motojima S. and Kohno M., Thin Solid Films, 137(1986)59.

Münz W.D., Goebel J. and Hofmann D., Proc. 7 th ICVM, 1982, Tokyo, Japan (a).

Münz W.D., Hofmann D. and Hartig K., Thin Solid Films, 96(1982)79 (b).

Perry A.J., Thin Solid Films, 146(1987)165.

Peterson J.R., J. Vac. Sci. Technol., 11(1974)715.

Powell C.F., Oxley J.H. and Blocher J.M., eds., Vapor Depsition, J. Wiley, 1966.

Sato T., Tada M. and Huang Y.C., Thin Solid Films, 54(1978)61.

Satou M., Andoh Y., Ogata K., Suzuki Y., Matsuda K. and Fujimoto F., Jpn. J. Appl. Phys., 24(1985)656.

Schintlmeister W., Pacher O., Pfaffinger K. and Raine T., J. Electrochem. Soc., 123(1976)924.

Sproul W.D., Thin Solid Films, 107(1983)141.

Sundgren J.-E., Johansson B.-O. and Karlsson S.E., Thin Solid Films, 105(1983)353 (a).

Sundgren J.-E., Johansson B.-O., Karlsson S.-E. and Hentzell H.T.G., Thin Solid Films, 105(1983)367 (b).

Sundgren J.-E., Johansson B.-O., Hentzell H.T.G. and Karlsson S.-E., Thin Solid Films, 105(1983)385 (c).

Sundgren J.-E., Thin Solid Films, 128(1985)21.

Synielnikowa W., Niemyski T., Panczyk J. and Kierzek-Pecold E., J.Less-Common Met., 23(1971)1.

Takahashi T. and Suzuki Y., J.Chem.Soc.Japan, Industr. Chem., 30(1974)1043.

Takahashi T. and Itoh H., J. Electrochem. Soc., 124(1977)797.

Telama A., Torkkell K., Mantyla T. and Kettunen P., J. Mater. Sci., 22(1987)2893.

Ting C.Y., J.Vac.Sci.Technol., 21(1982)14.

Tsao C.J., Du Y.S. and Miao H.F., Proc. 10th Intern. CVD Conf., Cullen G.W., ed., The Electrocehm. Soc., Pennington, N.J., USA 1987, p. 81.

Valvoda V. and Musil J., Thin Solid Films, 149(1987)49.

Valvoda V., Kuzel R.Jr. and Cerny R., Thin Solid Films, 156(1988)53 (a).

Valvode V. Cerny R. and Kuzel R.Jr., Thin Solid Films, 158(1988)225 (b).

Wendler B., Thin Solid Films, 141(1986)223.

Wittmer M. and Melchior H., Thin Solid Films, 93(1982)397.

Yamashina T. and Suzuki M., Proc. ICMC, 1983, San Diego, USA.

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